# Supporting Information

## Hierarchical Microspheres Comprised of Mn-Doped CoP Nanosheets for Enhanced Oxygen Evolution

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#### 1. Experimental

#### 1.1. Materials

Analytical grade ethanol, cobalt (II) acetate tetrahydrate ( $Co(CH_3COO)_2 \cdot 4H_2O$ , 99.5%), manganese acetate tetrahydrate ( $Mn(CH_3COO)_2 \cdot 4H_2O$ , 99%), ethylene glycol ( $C_2H_6O_2$ ), polyethylene glycol and sodium hypophosphite ( $NaH_2PO_2$ , 99.0%) were purchased from Aladdin Ltd. (Shanghai, China). Deionized water from Milli-Q System (Millipore, Billerica, MA) was used in all experiments. All the chemicals used in this experiment were used without further purification.

1.2. Synthesis of CoMn<sub>2</sub>O<sub>4</sub> hierarchical microspheres

In a normal procedure, 0.5 mmol  $Co(CH_3COO)_2 \cdot 4H_2O(0.1245 \text{ g})$ , 1 mmol  $Mn(CH_3COO)_2 \cdot 4H_2O(0.245 \text{ g})$  and 1g polyethylene glycol were dissolved in 35 ml ethylene glycol under ultrasound to form a clear solution at room temperature. After forming homogeneous solution by magnetic stirring for 10 min, the resulting solution was transferred to 50 ml Teflon-lined stainless-steel autoclaves and then heated at 200°C for 6 h. After cooled in air, the resulting precipitates were separated via centrifugation and further purified by an ethanol-water mixture for several times. The product was dried under vacuum at 60°C and finally calcined at 600°C for 3 h.

#### 1.3. Synthesis of Co<sub>3</sub>O<sub>4</sub>

In a normal procedure, 1.5 mmol  $Co(CH_3COO)_2 \cdot 4H_2O$  (0.369 g) and 1 g polyethylene glycol were dissolved in 35 ml ethylene glycol under ultrasound to form a clear solution at room temperature. After ultrasound for 10 min, the resulting homogeneous solution was transferred to 50 ml Teflon-lined stainless-steel autoclaves and then heated at 200°C for 6 h. After cooled in air, the resulting precipitates were separated via centrifugation and further purified by an ethanol-water mixture for several times. The product was dried under vacuum at 60 °C and finally calcined at 600 °C for 3 h.

#### 1.4. Synthesis of Mn-CoP hierarchical microspheres

In a normal procedure,  $CoMn_2O_4$  (20 mg) and  $NaH_2PO_2$  (200 mg) were placed in the porcelain boat, separately. The  $NaH_2PO_2$  was located at the upstream. The boat was then heated at 350°C for 2 h under nitrogen with a heating rate of 5°C min<sup>-1</sup>, and then naturally cooled to room temperature.

#### 1.5. Synthesis of CoP

In a normal procedure,  $Co_3O_4$  (20 mg) and  $NaH_2PO_2$  (200 mg) were placed in the porcelain boat, separately. The  $NaH_2PO_2$  was located at the upstream. The boat was then heated at 350°C for 2 h under nitrogen with a heating rate of 5°C min<sup>-1</sup>, and then naturally cooled to room temperature.

#### 1.6. Characterization

Powder X-ray diffraction patterns (PXRD) of samples were recorded using a Rigaku Miniflex-600 with a Cu K $\alpha$  radiation (Cu K $\alpha$ ,  $\lambda = 0.15406$  nm, 40 kV and 15 mA). Transmission electron microscopy (TEM) was carried out by a JEM-2100F equipped with energy dispersive spectrometer (EDS) analyses at 100 kV and the EDS elemental mapping was operated at 200 kV.

The scanning electron microscope (SEM) was performed on SU8020 (Hitachi) SEM. The XPS was collected on scanning X-ray microprobe (ESCALAB250Xi, Thermo, United States) using Al K $\alpha$  radiation and the C1s peak at 284.6 eV was used as internal standard. Elemental analysis of Co, Mn, and P in the samples was detected by an Optima 7300 DV inductively coupled plasma-mass spectrometry (ICP-MS). Specific surface areas were computed from the results of N<sub>2</sub> physisorption at 77 K (Micromeritics ASAP 2020) by using the Brunauer–Emmet–Teller (BET) and Barrett–Joyner–Halenda (BJH) method.

#### 1.7. Electrochemical measurements

All the electrochemical experiments were conducted on the electrochemical workstation (CHI 760E) in a three-electrode system in 1.0 M KOH solution at room temperature. All samples were tested on the glassy carbon electrode (GCE, 0.196 cm<sup>2</sup> in area) as the working electrode, Ag/AgCl as the reference electrode and a Pt wire as the counter electrode. Catalysts (4 mg) were dispersed in 960  $\mu$ l ethanol and 40  $\mu$ l 5% Nafion by sonication for 30 min. Then, 10  $\mu$ l well-dispersed catalysts (0.31 mg/cm<sup>2</sup>) were covered on GCE by drying naturally for test. The OER was conducted in O<sub>2</sub>-saturated 1.0 M KOH solution with a scan rate of 10 mV s<sup>-1</sup> at 1600 rpm on a rotating disk electrode. All potentials were referenced to a reversible hydrogen electrode (RHE) with iR correction. The R was referred to the ohmic resistance arising from the electrolyte/contact resistance of the setup, and measured by electrochemical impedance spectroscopy (EIS). EIS measurements were carried out from 100 kHz to 0.1 Hz with an amplitude of 5 mV at 0.6 V vs. Ag/AgCl on a rotation disk electrode at 1600 rpm.

The catalyst ink of RuO<sub>2</sub> sample was prepared by mixing 4 mg in 960  $\mu$ l ethanol and 40  $\mu$ l 5% Nafion solution by sonication for 30 min. Then, 10  $\mu$ l well-dispersed RuO<sub>2</sub> (0.20 mg/cm<sup>2</sup>) was covered on GCE by drying naturally for test.

The turnover frequency (TOF) of catalysts was further calculated based on the following standard equation:<sup>1</sup>

$$TOF = \frac{J * A}{4 * F * m}$$
(S1)

Here, J is the current density (A cm<sup>-2</sup>) at an overpotential of 0.35 V. A and m are the area of the electrode and the number of moles of the active materials that were deposited onto the electrode, respectively. F is the Faraday constant (96,485 C mol<sup>-1</sup>).

### 2. Supplementary Figures





Figure S1. XRD pattern of Mn-Co-EG.

Figure S2. Energy dispersive X-ray spectroscopy (EDS) of CoMn<sub>2</sub>O<sub>4</sub>.



**Figure S3.** (a)  $N_2$  adsorption/desorption isotherm (77K) curve of Mn-CoP hierarchical microsphere, (b) porous volume distributions of the pore size.



**Figure S4.** Energy dispersive X-ray spectroscopy (EDS) of Mn-CoP. The peak of Cu in the EDS spectra was from Cu grid.



**Figure S5.** SEM images of (a) Co-EG, (b)  $Co_3O_4$  and (c) CoP. TEM images of (d) Co-EG, (e)  $Co_3O_4$  and (f) CoP.



Figure S6. XRD patterns of CoP and Co<sub>3</sub>O<sub>4</sub>.



Figure S7. XPS survey spectra of Mn-CoP and CoP.



Figure S8. XPS spectra of (a) CoMn<sub>2</sub>O<sub>4</sub>, (b) Co 2p, (c) Mn 2p and (d) O 1s.

In Co 2p region, four distinct peaks are attributed to  $Co^{3+}$  (780.9 and 796.6 eV) and  $Co^{2+}$  (785.8 and 802.8 eV), respectively. In Mn 2p region, two peaks located at 642.5 eV and 653.6 eV correspond to Mn  $2p_{3/2}$  and Mn  $2p_{1/2}$ , respectively. Moreover, the Mn 2p peaks were further deconvoluted into two kinds of Mn components. The peaks located at 642.5 eV and 653.6 eV are ascribed to Mn<sup>3+</sup> while those located at 641.3 eV and 653.3 eV belong to Mn<sup>2+,2</sup> The O 1s peaks could be deconvoluted into parts: one peak at 531.4 eV correspond to the lattice oxygen in the spinel CoMn<sub>2</sub>O<sub>4</sub>, while the other peak at 530.2 eV is due to the typical metal–oxygen bonds.<sup>3</sup>



Figure S9. XPS spectra of (a)  $Co_3O_4$ , (b) Co 2p and (c) O 1s.

In Co 2p region, six distinct peaks can be assigned to  $Co^{3+}$  (778.8 and 793.7 eV),  $Co^{2+}$  (782.5 and 798.7 eV) and satellite peaks (786.8 and 803.6 eV).<sup>4</sup> In O 1s region, the peaks at 530.2 eV and 531.4 eV belong to surface lattice oxygen and adsorbed oxygen species.<sup>5</sup>



**Figure S10.** CV curves of (a) Mn-CoP, (b)  $CoMn_2O_4$ , (c) CoP, (d)  $Co_3O_4$  and (e)  $RuO_2$  measured in 1.0 M KOH solution at scan rates of 2 to 10 mV s<sup>-1</sup>. (f) The plot of the current density at 1.285 V versus the scan rate.



Figure S11. The electrochemical surface area (ECSA) of Mn-CoP, CoP, CoMn<sub>2</sub>O<sub>4</sub>, Co<sub>3</sub>O<sub>4</sub> and RuO<sub>2</sub>.

The electrochemical active surface area (ECSA) of the catalyst was estimated from the double-layer capacitance ( $C_{dl}$ ).<sup>6</sup> Therefore, the electrochemical capacitance was evaluated via cyclic voltammetry in the potential range of 1.25-1.29 V versus RHE. Each CV segment was swept three times at each scan rate (2, 4, 6, 8 and 10 mV s<sup>-1</sup>) before recording the CV curves shown in Figure S10). The capacitive currents were then analyzed at the potential of 1.285 V versus RHE, and plotted as a function of the scan rate (Figure S10f). The slope of the linear fit yields the specific capacitance of ~37.9, 2.4, 35.4, 3.9 and 16.6 mF cm<sup>-2</sup> for Mn-CoP, CoP, CoMn<sub>2</sub>O<sub>4</sub>, Co<sub>3</sub>O<sub>4</sub> and RuO<sub>2</sub>.

By considering the specific capacitance of an atomically smooth planar surface with a real surface area of 1.0 cm<sup>2</sup> and specific capacitance (Cs) generally within 20-60  $\mu$ F cm<sup>-2</sup> range alkaline media, the specific capacitance can be translated into the ECSA by calculation from the following equation. Herein, by using the midpoint specific capacitance of 40  $\mu$ F cm<sup>-2</sup>, the ECSA of Mn-CoP is determined as:

 $ECSA = C_{dl}/C_s = 37.9 \text{ mF cm}^{-2}/40 \mu \text{F cm}^{-2} \text{ per cm}^{2}_{ECSA} = 947.5 \text{ cm}^{2}$ (S2)



Figure S12. The turnover frequency (TOF) of Mn-CoP, CoP,  $CoMn_2O_4$ ,  $Co_3O_4$  and  $RuO_2$  at an overpotential of 0.35 V.



Figure S13. XRD patterns of Mn-CoP before and after OER durability test.



Figure S14. (a) TEM and (b) SEM images of Mn-CoP after OER durability test.

# 3. Supplementary Tables

Mn (at. %)	Co (at.%)	[Mn]/[Co]	[Mn]/[Mn+Co]	[Co]/[Mn+Co]
65.76	34.24	1.92	65.76	34.24

Table S1. ICP-MS analysis results of the element content of Mn, Co for Mn-Co-EG

Table S2. ICP-MS analysis results of the element content of Mn, Co for  $CoMn_2O_4$ 

Mn (at. %)	Co (at. %)	[Mn]/[Co]	[Mn]/[Mn+Co]	[Co]/[Mn+Co]
63.89	36.11	1.77	63.89	36.11

Table S3. ICP-MS analysis results of the element content of Mn, Co, and P for Mn-CoP

Mn (at. %)	Co (at. %)	P (at. %)	[Mn]/[Co]	[Mn]/[Mn+Co]	[Mn+Co]/[P]
28.81	23.29	47.90	1.24	0.55	1.09

**Table S4.** Comparison of the overpotentials at 10 mA cm<sup>-2</sup> compared to previously reported catalysts in 1.0 M KOH electrolyte

Electrocatalysts	Electrolyte	Overpotential (10 mA cm <sup>-2</sup> )	Reference
Mn-CoP	1 M KOH	285 mV	This work
RuO <sub>2</sub>	1 M KOH	330 mV	This work
Co <sub>3</sub> O <sub>4</sub>	1 M KOH	307 mV	4
$\beta$ -Ni(OH) <sub>2</sub> NPs-H <sub>2</sub>	1 M KOH	340 mV	7
Fe-CoO/C	1 M KOH	362 mV	8
CoMoO <sub>4</sub>	1 M KOH	312 mV	9
Co-CN SS	1 M KOH	290 mV	10
Fe <sub>1</sub> Co <sub>1</sub> -ONS	1 M KOH	308 mV	11
NiCoP / C	1 M KOH	330 mV	12
Mn-Cooxyphosphide	1 M KOH	370 mV	13
SnCoFe-Aron Ni foam	1 M KOH	270 mV	14
CoFeP	1 M KOH	340 mV	15
CoS <sub>2</sub>	1 M KOH	308 mV	16
CoO <sub>x</sub> -4h	1 M KOH	306 mV	17
CoP–TiO <sub>x</sub>	1 M KOH	337 mV	18
CoP NFs	1 M KOH	323 mV	19
CoP / NCS-400	1 M KOH	313 mV	20
CoP / VGNHs	1 M KOH	300 mV	21
CoP/CN@MoS <sub>2</sub>	1 M KOH	289 mV	22
O-CoP	1 M KOH	310 mV	23
CoP@NPC	1 M KOH	300 mV	24

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